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# Effect of Lignin Diffusion on Kraft Delignification Kinetics as Determined by Liquor Analysis. Part II: Theoretical Analysis

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## Abstract

This study provides the theoretical analysis of the effect of lignin diffusion on the kraft delignification kinetics of black spruce as determined by liquor analysis. The rate of lignin transport from wood chips to bulk liquor is modeled with an equation describing non steady-state, one-dimensional diffusion with an internal generation term from chemical reaction. An exact solution was derived for this equation. A program based on spreadsheet macro was developed to calculate the dissolved lignin-concentration profiles in the wood chips. It is found that the measured lignin concentration in cooking liquor can be accurately described by the diffusion model. The theoretical calculation confirms the experimental finding obtained that the effect of temperature on the lignin concentrations from liquor analysis could not be described by using the classical value of 134 kJ/mol for the activation energy for kraft cooking of black spruce. The activation energy measured experimentally is lower because diffusion has a stronger effect on the measured lignin-dissolution rate at higher temperatures. The model is also used to evaluate the lignin concentration profiles within wood chips and the bulk and intrachip lignin concentrations as a function of chip thickness and temperatures.

## Introduction

Our previous report presented an experimental evaluation of the effect of lignin diffusion on the kraft delignification kinetics of black spruce as determined by liquor analysis [1]. In the study, the measured lignin concentration in cooking liquor was compared to the values calculated by using the delignification kinetics expressed through the well-known "H" factor [2]. The comparison indicated that the effect of temperature on the lignin concentrations from liquor analysis could not be described by using the classical value of 134 kJ/mol for the activation energy for kraft cooking of black spruce. A lower value of activation energy gave a better fit to the data. It was concluded, therefore, that diffusion limitation played an important role in the delignification rate as measured by liquor analysis. The higher the reaction rate, the stronger the mass transfer limitation is. For example, the measured rate was more than two times lower than the theoretical value at 180°C. Based on the study, it was suggested that cooking temperature or chip thickness or both have to be significantly reduced to eliminate the diffusion effect on the measured rate.

This report is intended to provide the theoretical background and confirmation about the conclusion drawn from the experimental study, i.e., the lignin-dissolution rate measured by liquor analysis could be significantly affected by diffusion. The calculated lignin-diffusion rate is compared with the experimentally measured rate reported in the last report.

## Theory

### *Mathematical Model of Lignin Diffusion*

The rate processes involved in kraft cooking of wood chips are the same as most other liquid-solid reactions. Mobile reactants (hydroxide and hydrosulfide ions) first diffuse into the wood chips and then react with the "non mobile" lignin polymer. After the degradation reaction, soluble lignin macromolecules diffuse out of the fiber walls and the wood chips into the bulk cooking liquor (liquor outside the chips) to complete the kraft delignification process. External mass transfer, i.e., outside of wood chips in bulk liquor, is generally unimportant in laboratory digesters because of the high liquor-circulation rate, which is true for most industrial digesters as well.

Under certain conditions, e.g., thin chips and low temperature, diffusion of the cooking chemicals may not be a rate-limiting step for kraft delignification reaction [3, 4]. The degradation rate of the lignin polymer is then controlled by the kinetic rate. The dissolution rate of the dissolved lignin from the wood chips into the bulk liquor, however, can still be strongly influenced by the intrachip diffusion rate of lignin because the size of the degraded lignin molecules is still rather large, e.g., 5000 Dalton in average molecular weight [5-7]. This dissolution rate can be described by the equation for non steady-state, one-dimensional mass transfer with an internal generation term from the chemical reaction (assuming chip thickness is much smaller than width and height):

$$\frac{\partial C}{\partial t} = D(t)\frac{\partial^2 C}{\partial x^2} + R(t) \tag{1}$$

where $C$ is the concentration of the dissolved lignin, $D$ is the diffusion coefficient of lignin, and $R$ is the rate of dissolved lignin generated from chemical reaction. The initial and boundary conditions to solve the equation include:

$$C = C_0 = 0 \qquad \text{(at initial, } or\ t = 0\text{)} \tag{2}$$

$$\frac{\partial C}{\partial x} = 0 \qquad \text{(at chip center, or } x = l/2\text{)} \tag{3}$$

$$C_0 = C_l = C_b \qquad \text{(at chip edge, or } x = 0,\ l\text{)} \tag{4}$$

where $l$ is the thickness of the chip. Since the diffusion coefficient, $D$, the lignin degradation rate, $R$, and the bulk concentration of dissolved lignin, $C_b$, are functions of time, equation (1) cannot be solved analytically.

*Analytical Solution*

If a very small time interval, $\Delta t$, is considered, all three parameters above can be treated as constants, $D_t$, $R_t$, $C_{b,t}$, at a given time. In this situation, equation (1) becomes:

$$\frac{\partial C}{\partial \tau} = D_t\frac{\partial^2 C}{\partial x^2} + R_t \tag{5}$$

where $\tau$ is the time parameter within the $\Delta t$. The initial and boundary conditions for equation (5) are

$$C = f(x) \qquad (\tau = 0,\ 0 < l < l) \tag{6}$$

$$C_0 = C_l = C_{b,t} \qquad \text{(at chip edge, or } x = 0,\ l\text{)} \tag{7}$$

For this problem with the above inhomogeneous boundary condition, an analytical solution is obtained in this work, which is not found in the classical textbooks dealing with mathematics of diffusion and heat conduction [8, 9]. The procedure is briefly outlined here. First, let the solution $C(x, \tau)$ consist of a steady-state solution $v(x)$ and a transient solution $w(x, \tau)$, i.e.,

$$C(x,\tau) = v(x) + w(x,\tau) \tag{8}$$

$$D_t\frac{\partial^2 v}{\partial x^2} + R_t = 0 \tag{9}$$

$$\frac{\partial w}{\partial \tau} = D_t \frac{\partial^2 w}{\partial x^2} \tag{10}$$

To solve for $v(x)$, let $\frac{\partial C}{\partial \tau} = 0$ and applying condition $v(0) = v(l) = C_{b,t,t}$, hence

$$v(x) = \frac{R_t}{2D_t}(l - x)x + C_{b,t} \tag{11}$$

For the transient solution $w(x, \tau)$, the homogeneous equation (9) is solved by separation of variables, Fourier series techniques, and eigen functions evaluation with the initial condition, $w(x,0) = f(x) - v(x)$, and the boundary condition, $w(0,\tau) = w(l,\tau) = 0$. The transient solution $w(x, \tau)$ can be expressed as

$$w(x,\tau) = \sum_{n=1}^{\infty} C_{n,t} \exp\left(-\frac{D_t n^2 \pi^2}{l^2}\tau\right) \sin\left(\frac{n\pi x}{l}\right) \tag{12}$$

where

$$C_{n,t} = \frac{2}{l}\int_0^l \left[ f(x) - \left(\frac{R_t}{2D_t}(l - x)x + C_{b,t}\right)\right] \sin\left(\frac{n\pi x}{l}\right) dx \tag{13}$$

After substituting equations (11), (12), and (13) into equation (8), we have the solution for equation (5). The general solution at the end of each small time interval, $\Delta t$, and any given $t$ and $x$ is

$$C(x,t) = \frac{R_t}{2D_t}x(l - x) + C_{b,t} + \sum_{n=1}^{\infty} C_{n,t} \exp\left(-D_t \frac{n^2 \pi^2 \Delta t}{l^2}\right) \sin\left(\frac{n\pi x}{l}\right) \tag{14}$$

By using equation (14), the dissolved lignin-concentration profile across the chip thickness during a kraft cook can then be simulated by solving for the lignin profile over a small time step, $\Delta t$, and using this profile as the initial $f(x)$ function in order to solve for the lignin profile in the next time step. This process is repeated until the desired time is reached. Because of the complexity of the exact solution (equation (14)) and the associated parameters (defined later in equations (15)-(19)), a macro program (model) had to be written in Excel spreadsheet to accomplish this numerical calculation. Since the quantities that the model solves for involve infinite series (equations (14), (16), and (17)), care must be taken to ensure that convergence of the infinite series is reached, which may require a large value of $n$, depending on the dimensionless number $Dt/l^2$.

Calculation of equation (14) requires knowing the parameters, $D_t$, $R_t$, $C_{n,t}$, $f(x)$, and $C_{b,t}$, which are further described in the following section. Among them, the bulk lignin concentration, $C_{b,t}$, as a function of time is the most important parameter to examine since it can be compared with the experimentally measured values.

*Solution of $C_{n,t}$*

The analytical solution involves the term $C_{n,t}$ (equation (13)). It has a constant value for each value of n in the infinite series. If *f(x)* is complex, the integral part containing *f(x)* has to calculate via numerical integration method. The exact solution is derived for the problem in this study. This involves substituting the exact equation for *f(x)* into the $C_{n,t}$ expression (equation (13)). The exact equation for f*(x)* is *C(x,t-Δt)*, that is, the equation (14) for *C(x,t)* using the values of $D_{t-\Delta t}$ , $R_{t-\Delta t}$ etc... from the previous time step. $C_{n,t,}$ can, therefore, be solved analytically, and is found to be:

$$C_{n,t} = \left(\frac{R_t}{D_t} - \frac{R_{t-\Delta t}}{D_{t-\Delta t}}\right)\left(\frac{2l^2}{(n\pi)^3}\right)\left[(-1)^n - 1\right] + (C_{b,t} - C_{b,t-\Delta t})\left(\frac{2}{n\pi}\right)\left[(-1)^n - 1\right] + C_{n,t-\Delta t}\exp\left(-D_{t-\Delta t}\frac{n^2\pi^2\Delta t}{l^2}\right) \quad (15)$$

*The Boundary Condition*

The boundary condition, $C_{b,t}$, can be obtained from the mass balance, i.e., the mass of dissolved lignin removed from the chip equals the mass increased in bulk liquor over the interval *Δt*:

$$C_{b,t} = C_{b,t-\Delta t} + \frac{V_{void}}{V_{bulk}}\left(R_t - \left(C_{v,averag,t} - C_{v,average,t-\Delta t}\right)\right) \quad (16)$$

where $V_{void}$ and $V_{bulk}$ are the liquor volumes in chip void and in bulk, respectively. $C_{v,average,t}$ is the integral average value of the concentration profile over the chip and can be solved from equation (14):

$$C_{v,average,t} = \frac{\int_0^l C(x,t)dx}{l} = \frac{R_t l^2}{12D} + C_{b,t} + \sum_{n=1}^{\infty} C_{n,t}\exp\left(-D_t\frac{n^2\pi^2\Delta t}{l^2}\right)\left(\frac{1}{n\pi}\right)\left[1-(-1)^n\right] \quad (17)$$

*Kinetic Rate of Dissolved-Lignin Generation $R_t$*

The procedure used in Part I of this study is used to estimate the kinetic rate at different temperatures [1]. The measured rate at the lowest temperature, 155°C, which is the least affected by diffusion, is used as the basis rate. The increased kinetic rate at higher temperatures is calculated from the rate at 155°C corrected with the Arrhenius equation and the activation energy, *E*, of 134 kJ/mol (32 kcal/mol) used in the "H" factor calculation [2]:

$$\left.\frac{dL}{dt}\right|_T = \left.\frac{dL}{dt}\right|_{155^\circ C} \bullet \exp\left[\frac{E}{R}\left(\frac{1}{428} - \frac{1}{T}\right)\right] \quad (18)$$

where $(dL/dt)_T$ is the rate at temperature $T$, and $(dL/dt)_{155°C}$ is the rate at 155°C. To avoid the error from the transition from initial to bulk delignification phase, the rate is calculated at a given lignin content on wood using the rate at 155°C at the same lignin content on wood.

*Diffusion Coefficient $D_t$*

An average diffusion coefficient based on an average molecular weight of 5,000 Dalton is calculated from the Stokes Einstein equation and adapted to different temperatures by an Arrhenius expression [3]:

$$D_t = \frac{kT_{293}}{6\pi\mu r}\left(\frac{T(t)}{T_{293}}\right)^{1/2} \exp\left(\frac{22.4}{0.0083146}\left(\frac{1}{T_{293}} - \frac{1}{T(t)}\right)\right) \qquad (19)$$

Where $k$ is Boltzmann's constant (1.38 x $10^{-23}$ J/K). $r$ is the radius (=1.2 nm) of the lignin molecule at 5,000 Dalton, which is calculated based on a correlation in the reference [5-6]. $\mu$ is the liquor viscosity at 20°C.

## Results and Discussion

*Model Validation*

The exact solution of equation (5) requires that the time step is small enough so that the parameters, like $D_t$, $R_t$, and $C_{b,t}$, can be treated as constants. When the time step was reduced to 3 seconds from 6 seconds, the difference of the calculated concentrations was less than 1%. Most of the results presented were obtained using 6 seconds as the time step.

Figure 1 shows the concentrations of the dissolved lignin in the cooking liquor as a function of cooking time obtained at five different cooking temperatures. The symbols are the measured values described in the last paper. The lines represent the calculated concentrations of the bulk liquor from the model. The chip thickness used was 5 mm in all five cases. The agreement between the model prediction and the experiments are very good. At lower temperatures, i.e., 155 and 160°C, the model gives slightly lower values at about 90 to 150 minutes when the kinetic rate reached the highest level. At this time range, the model probably overestimated the diffusion effect. One of the reasons for this discrepancy is the chip thickness of 5 mm is probably higher than the average chip thickness. At above 200 minutes, the agreement becomes excellent. On the other hand, the model gives slightly higher values at the later stage of cooking for the two cooks at the higher temperatures, i.e., 175 and 180°C, indicating that the model underestimated the diffusion effect. The diffusion coefficient used in this calculation was only corrected for the temperature effect, but not corrected for the effect of the viscosity increase of black liquor from the higher solids content. The actual diffusion coefficient should be lower at the higher solids content. Since the diffusion limitation is much more serious at the higher cooking temperatures, dissolved lignin must have greatly accumulated within the

chips. The calculated results would have greater dependence on the accuracy of the diffusion coefficient.

*Temperature Effect - Analysis Based on the "H" Factor Theory*

It was derived in the first part of this study that the dissolved lignin concentration of the bulk liquor plotted against "H" factor should be independent of cooking temperature if the lignin dissolution rate depends on the kinetic delignification rate and is not affected by diffusion. However, the experimental data could not fall onto the same line when the "H" factor is calculated from the activation energy of 134 kJ/mol (32 kcal/mol). Values higher than 134 kJ/mol (32 kcal/mol) led to even higher degrees of divergence while lower values improved convergence. An activation energy of 100.5 kJ/mol (24 kcal/mol) gave the highest degree of convergence. The same excess is performed on the calculated bulk lignin concentrations. The results are shown in Figure 2. When $C_b$ is plotted against the standard "H" factor, the lines are separated from each other in the large part of middle range where the delignification rate is high. As was found for the experimental data, the lower activation energy, 24 kcal/mol, led to better convergence of the lines. The results shown in Figure 2 are almost the replicate found for the measured data, confirming that the rate of lignin dissolution can be significantly affected by the diffusion rate.

*Concentration Profiles within the Chips*

In addition to the bulk lignin concentration, the model solution also gives the dissolved lignin-concentration profiles across the chips and the average concentrations. Figure 3 shows the concentration profiles across the chips for the five cooks at different temperatures. The thickness used in the calculate was 5 mm. The time interval between each profile is 20 minutes for the first four cooks and 10 minutes for the cook at 180°C. The lower values at the boundary indicate that the accumulation of the dissolved lignin within the chips already started at the early part of cooking. The accumulation reached the highest level at 80 to 100 minutes. At the highest temperature, i.e., 180°C, the concentration at the center is about twice that at the edge at 90 minutes. Diffusion limitation cannot be neglected even at 155°C during the bulk delignification phase.

When the average intrachip concentrations, $C_{v,a}$, are compared with the bulk liquor concentrations, $C_b$, in Figure 4, the same conclusion can be drawn, i.e., the bulk concentration does not represent the true kinetic rate of delignification under certain conditions. Therefore, this result demonstrates that diffusion limitation is difficult to eliminate by simply reducing the reaction rate with lower temperatures.

*The Effect of Chip Thickness*

The much more effective way to minimize the diffusion limitation is to reduce the chip thickness. The effect of chip thickness on lignin-dissolution rate is examined with the present model. The temperature of the cook is 170°C. In addition to the 5-mm chip, shown in Figure 3, the simulation was performed with five other thicknesses: 1, 2, 3, 7, and 10 mm. The calculated dissolved lignin-concentration profiles are shown in Figure 5. The time interval between each profile is 20 minutes. The dissolved lignin accumulation

within the thick chips, e.g., 7- and 10-mm chips, is very significant. At 3-mm thickness, the accumulation is not negligible when the kinetic rate is the highest at about 100 minutes. The difference of the concentrations between the center and the edge, i.e., the bulk, at 90 minutes is still more than 20%. As the chip thickness is further reduced to 2 and 1 mm, the effect of diffusion rate on the bulk lignin concentration becomes less important. The center value at the highest kinetic rate is about 15% different from the bulk concentration. At other times, the difference is much smaller.

The calculated rate of lignin dissolution also confirms that when chip thickness is reduced to 2 mm or below, the lignin dissolution rate is not significantly affected by the diffusion rate. At 2 mm, the dissolution rate is only about 7% different from the kinetic rate at the highest kinetic rate, while at 1 mm, the difference is further reduced to 2%. Therefore, delignification kinetics of a kraft cooking could be obtained from dissolved-lignin analysis in bulk liquor if the kraft cooking is conducted with 1-mm-thick wood chips and at temperatures not higher than 170°C. Other restrictions are that wood chips should be well impregnated with the cooking liquor, and that the cooking chemical concentration should not be too high to lead to a much higher kinetic rate. With 2-mm-thick wood chips, the error could still be acceptable.

## Conclusions

An exact solution was derived for the partial differential equation describing the rate of lignin transport from wood chips to bulk liquor. To calculate the numerical results, a simulation program based on spreadsheet macro method was developed to obtain the numerical values. The numerical results indicate that the measured lignin concentration in cooking liquor can be accurately described by the diffusion model. The theoretical analysis confirms the finding obtained experimentally that the rate of lignin dissolution from liquor analysis measured at high temperatures was strongly hindered by the diffusion process. Thus, a lower value was measured for the apparent activation energy. The exaction solution derived in this work can be a useful tool to establish the conditions required for wood delignification kinetic studies based on bulk pulping liquor analysis. For example, for softwood kraft pulping, it is possible to measure the true kinetic rate from liquor analysis if the wood chip is not too much thicker than 1 mm and the temperature is not higher than 170°C.

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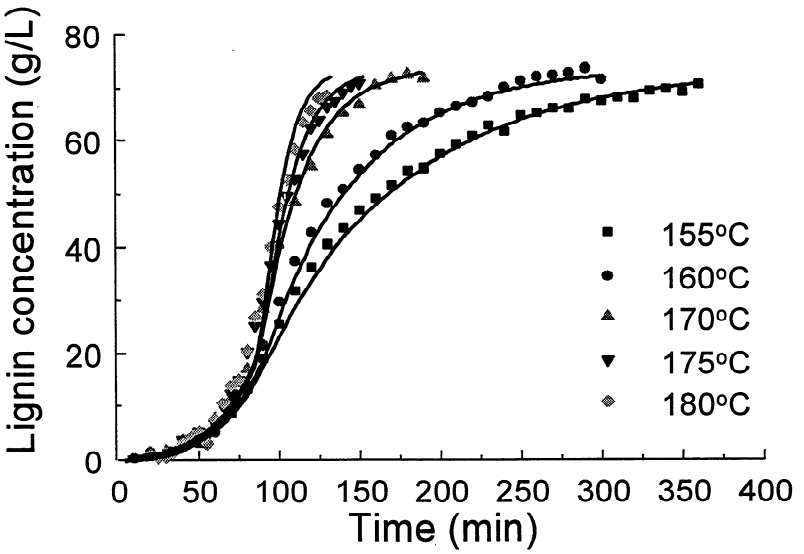


Figure 1. The concentration of the dissolved lignin in the bulk cooking liquor as a function of cooking time and cooking temperature. The symbols are measured by ATR-FTIR technology [1] during cooking, and the lines are calculated using the diffusion model. The agreement is relatively good.

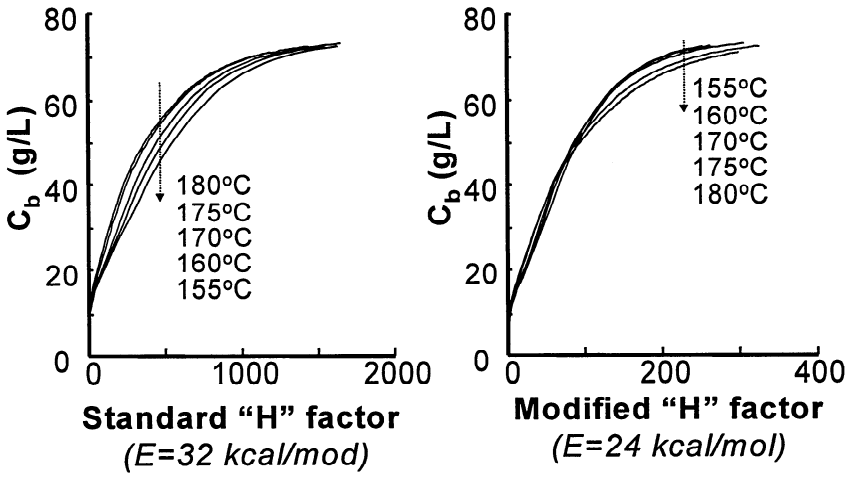


Figure 2. The calculated lignin concentration in the bulk cooking liquor plotted against standard "H" factor (left) and against modified "H" factor (right).

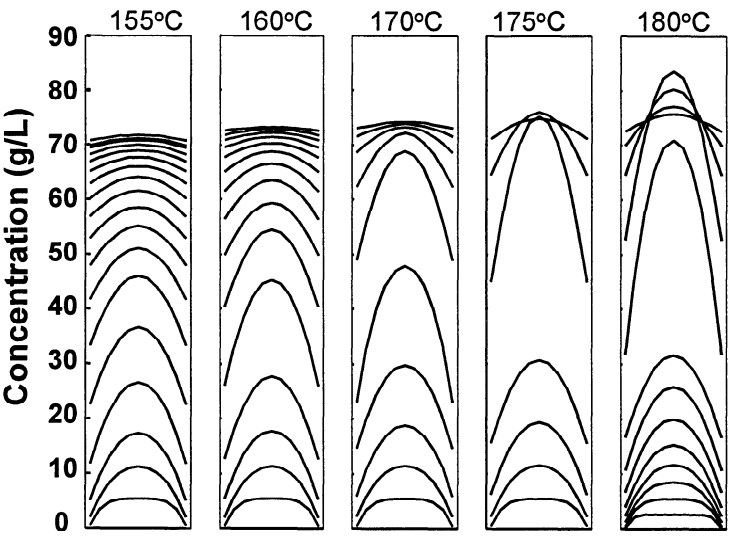


Figure 3. Dissolved lignin concentration profiles within the 5-mm chips at different cooking temperatures. Time interval between the profiles is 20 minutes for the four cooks at lower temperatures and 10 minutes for the cook at 180°C.

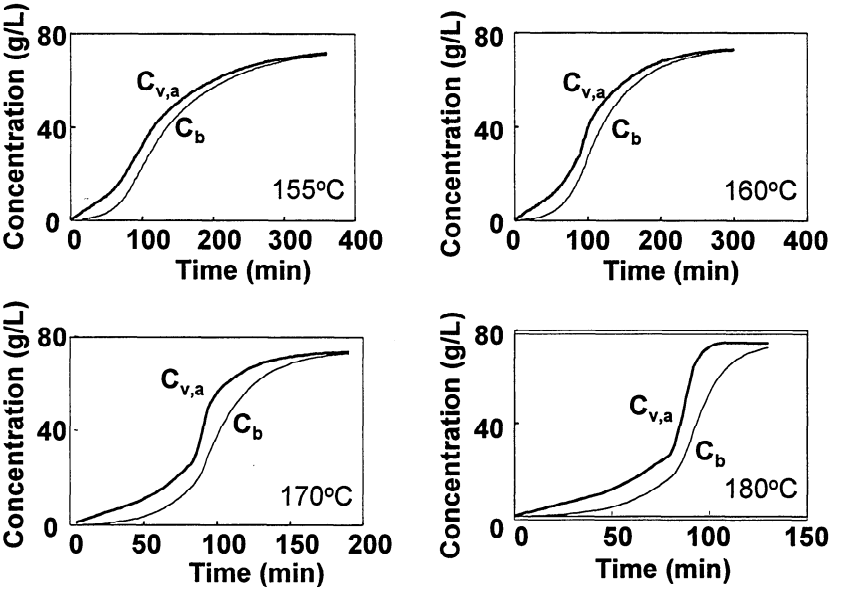


Figure 4. The average concentration of dissolved lignin within chips is compared with the concentration in bulk liquor as a function of cooking time. The chip thickness is 5 mm. Lignin concentration within the chips is significantly higher even at 155°C

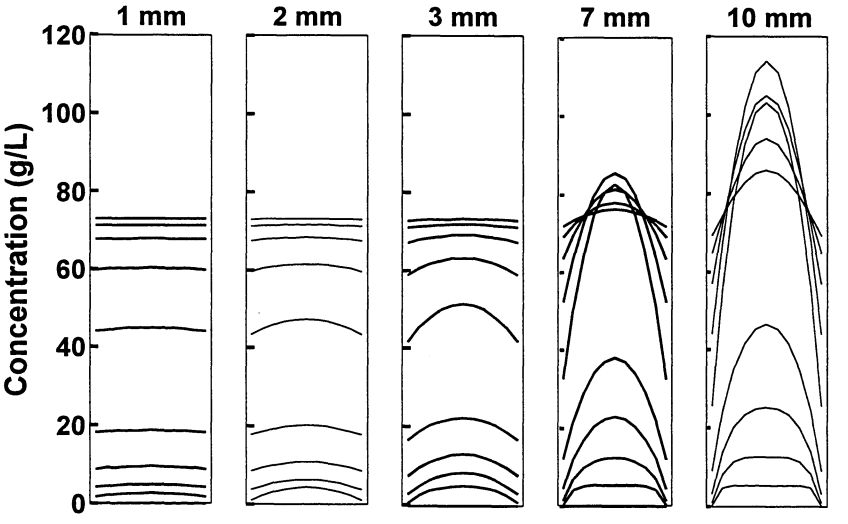


Figure 5. Dissolved lignin-concentration profiles within wood chips for five different thicknesses: 1, 2, 3, 7, and 10 mm. The cooking temperature is 170°C. Time interval between the profiles is 20 minutes. The diffusion process has negligible effect on the rate of delignification from the bulk liquor when the chip thickness is reduced to 1 mm.